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Zeolite Thin Film-Coated Long Period Fiber Grating Sensor for Measuring Trace Chemical

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Abstract: This paper reports the development of a new zeolite thin film-coated long period fiber grating (LPFG) sensor for direct measurement of trace organic vapors. The sensor was fabricated by growing pure silica MFI-type zeolite thin film on the optical fiber grating by *in situ* hydrothermal crystallization. The sensor measures chemical vapor concentration by monitoring the molecular adsorption-induced shift of LPFG resonant wavelength (λ_R) in near infrared (IR) region. Upon loading analyte molecules, the zeolite's refractive index changes in the close vicinity of the fiber index where the LPFG has a large response to achieve high sensitivity.

OCIS code: (060.2370) Fiber optics sensors.

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1. Introduction

In the last several years, the development of compact and sensitive fiber optic chemical sensors (FOCS) have been attracting increasing interests for broad applications ranging from detecting DNA to measuring gas molecules and ions in liquid. Different fiber structures and sensing mechanisms may be employed in FOCS among which the LPFG [1] provides new opportunities to develop refractive index sensors for measuring chemical concentration with high sensitivity [2, 3].

The LPFG is obtained by inscribing periodic index perturbations into the core of an optical fiber by laser irradiation. Lights of certain wavelengths (i.e. resonant wavelength, λ_R) are coupled from core mode to cladding modes when propagating through the LPFG. The λ_R is dependent upon both the fiber physical parameters and the optical properties of the medium surrounding the LPFG [4]. For a given LPFG with fixed fiber and grating parameters, the λ_R varies when the refractive index of the surrounding medium changes. Thus, LPFG-based sensors can be developed for direct or indirect measurement of chemical concentrations which determine the surrounding refractive index.

The direct measurement is conducted by monitoring the refractive index of the analyte-containing samples surrounding the bare LPFG [5, 6]. The indirect measurement is realized by monitoring the refractive index of an overcoat on the LPFG. The optical properties of this overcoat change upon interacting with the analyte molecules [7, 8]. For film-coated LPFG sensors, the selection of coating material is critical to the sensitivity. Theoretical models have been established to elucidate the effects of various structural and optical properties of the LPFG and the ambient or overcoat on the transmission spectra that can guide the development of LPFG sensors [3, 8-11].

The sensitivity of a film-coated LPFG sensor (Fig. 1) depends on the comparison between the refractive indices of the overcoat (n_{ov}) and the fiber cladding (n_{cl}). For overcoats with nanometer scale thickness, the sensor sensitivity is also strongly dependent upon the film thickness and the refractive index of the coating [8, 12, 13]. When $n_{ov} < n_{cl}$, the total internal reflection cladding mode can be well described by a three-layer model [10]. In case of $n_{ov} \geq n_{cl}$, a thin coating is able to favor the transition from cladding guided modes to overlay guided modes, causing a strong re-organization of the cladding modes [14]. Consequently, the sensitivity of the LPFG sensor strongly depends on the thickness and refractive index of the overlay layer.

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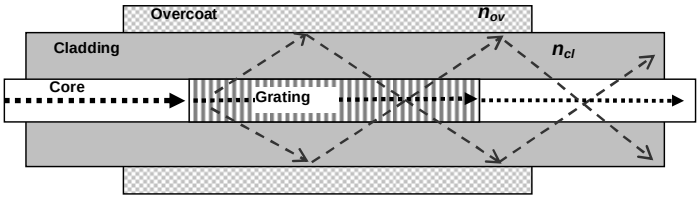

Fig. 1. Schematic showing cladding mode of LPFG with a film overcoat.

At $n_{ov} < n_{cl}$, the λ_R experiences a blue shift (decreasing) when n_{ov} increases. The λ_R shifts sharply as n_{ov} approaches n_{cl}, e.g. ~$1.3<n_{ov}<n_{cl}$ (n_{cl} ~1.46 for fused silica fiber) [2, 15]. With the current accuracy of wavelength measurement (1 pm), the cladding mode LPFG sensors are expected to have sensitivity to detect a n_{ov} change of 10^{-8} ~ 10^{-9} when n_{ov} is in the close vicinity of n_{cl} [2, 3, 8].

Zeolites are crystalline aluminosilicate materials possessing a unique combination of chemical and optical properties that is ideal for developing various optical chemical sensors [16-18]. The uniform molecular scale pore size and enormous surface-to-mass ratio make zeolites ideal sorbents for selective molecular adsorption. The pore size and structure as well as the adsorbing property of zeolites can be finely tuned by various modifications to further improve the selectivity of molecular adsorption [19-21].

The adsorbed analyte molecules are organized and aligned in the nanoscale zeolite pores due to spatial confinement and guest(molecule)-host(zeolite) interactions. Loading and unloading sorbate molecules can thus alter the optical and structural properties of zeolite that can be effectively examined by various optical methods [18]. Thereby, zeolites with multidimensional functions as an effective sample concentrator and optical probe have the potential for developing a variety of optical chemical sensors.

However, developing zeolite-based optical chemical sensors is still in the very early stage because of the difficulties associated with integrating zeolite with operational optical devices and the lack of fundamental understanding on the optical behavior of zeolite guest-host systems. Recently, we successfully synthesized highly coherent silicalite (i.e. pure silica MFI zeolite) thin films on straight cut endfaces of single mode optical fibers [22]. The endface-coated zeolite-fiber device was used to investigate the relationship between zeolite refractive index and organic sorption level by an interferometric method [23, 24].

Silicalite is an organophilic material with an effective pore size of ~6 Å and a specific surface area of ~500 m^2/g. It preferentially adsorbs organic molecules with kinetic diameters smaller than the zeolite pore size. The silicalite refractive index was found to increase from 1.3361 in pure N_2 to 1.4020 in 5353 ppm isopropanol vapor in N_2 [24]. This particular range of refractive index is desirable for constructing highly sensitive, film-coated LPFG sensors. In this study, we demonstrate a silicalite thin film-coated LPFG sensor for highly sensitive detection of organic vapors.

2. Experimental

2.1. Synthesis of zeolite film on the LPFG

In this work, we used a high performance LPFG made from Corning SMF-28 singlemode fiber via point-by-point CO_2-laser irradiation [25]. The LPFG had a period of 520 μm and a total grating length of ~5 cm. The resonance peak in the wavelength range of 1500-1650 nm is a result of light coupling from core mode to LP_{05} cladding mode. In general, the sensitivity depends on the order of the cladding mode. A higher order will result in a higher sensitivity. The LPFG was tested to be stable when annealing at 550°C in air for 200 hours. Such thermal stability is necessary because the silicalite-coated LPFG requires activation by calcination at >400°C to remove the structure directing agent (SDA) from the as-synthesized zeolite pores.

The silicalite film was grown directly on the LPFG cylindrical surface by *in situ* crystallization from an aluminum-free precursor solution using tetrapropylammonium ion

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(TPA^+) as SDA. The synthesis solution was prepared by mixing 11.3 ml (1M) of TPAOH (tetrapropylammonium hydroxide) (1M, Aldrich), 20.4 ml of TEOS (tetraethyl orthosilicate) (98%, Acros), and 60 ml of H_2O [22]. This particular precursor was found to be chemically friendly to the fiber surface due to its low alkalinity and high organic concentration. The mixture was vigorously stirred at 50°C for 3 hours. The resultant clear solution was transferred into a Teflon-lined stainless steel synthesis vessel.

The synthesis vessel had a tubular geometry with a 3/4″ inner diameter and a total length of 13 cm. About 13 cm of the fiber including the stripped grating segment was mounted in the vessel. The fiber was positioned with the grating section located in the middle of the tube (vessel) length. The vessel was then sealed and placed vertically in an oven. The hydrothermal synthesis was conducted at 180°C under autogeneous pressure for 4 hours. After the hydrothermal treatment, the zeolite-coated LPFG was rinsed with deionized water and then dried and fired at 500°C in air for 2 hours to remove the TPA SDA. The morphology and thickness of the zeolite film were examined by a scanning electron microscope (SEM).

2.2. Test for organic vapor detection

The high temperature sensor activation and room temperature (i.e. 22°C) chemical detection test were performed with an apparatus shown in Fig. 2. The zeolite-coated LPFG segment was hosted in a 1/8″–I.D. stainless steel tube, which is placed horizontally in a tubular furnace. The two ends of the stainless steel tube were connected to the sample gas supply system and ventilation, respectively. The concentration of the organic vapor was calculated from the vapor pressure at 0°C and the diluting air flow rates, which were varied to control the vapor concentration.

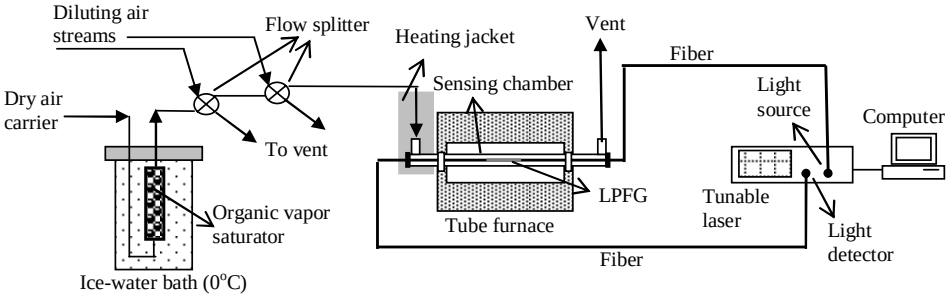

Fig. 2. Schematic diagram of the sensor testing system.

The transmission spectrum was obtained in a wavelength range from 1510 to 1640 nm. The source light was provided by a tunable laser equipped with a laser power detector (Agilent 8164A) and a computer data acquisition system. A wavelength increment of 0.1 nm and a dwelling time of 1 second were used in the organic sensing experiments. The calcination for sensor activation was done by the following program: heating up to 500°C at a rate of 4°C/min, holding at 500°C for 120 min, and then cooling down to room temperature at a rate of 2.5°C/min.

3. Results and discussion

Figure 3 shows the SEM images of the silicalite-LPFG. The images indicate that a continuous, well inter-grown zeolite film formed on the cylindrical LPFG surface although the outer surface had a discontinuous coverage of zeolite crystals. The thickness of the continuous zeolite layer was about ~10 μm as estimated from the SEM image. The crystals in the continuous zeolite layer appeared to be primarily *b*-oriented, which has straight channels with diameter of ~6 Å. Although there were isolated crystals on the coating surface, the film was dense and defect-free near the fiber-zeolite interface. The cladding modes are well confined by this defect-free interface. As a result, the rough outer surface and the variation of the coating thickness had very little impact on the sensitivity characteristics.

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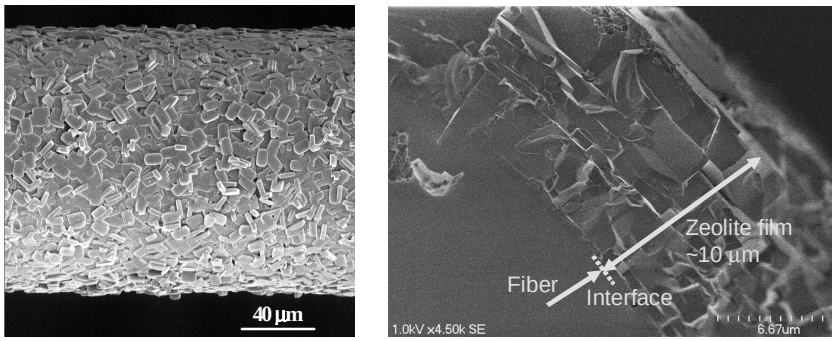

Fig. 3. SEM pictures of the zeolite-LPFG surface (left) and fracture cross-section (right).

After the thermal activation, the MFI zeolite-LPFG sensor was tested for detection of low concentration isopropanol and toluene vapors in air. The measurements were conducted at room temperature under atmospheric pressure. Figures 4 and 5 present the results of the vapor detection tests. For both isopropanol and toluene vapors, increasing the vapor concentration caused λ_R shift toward smaller wavelength. Such a shift of λ_R is resulted from the increase of zeolite film refractive index induced by the increasing sorption of organic molecules into the zeolite cavity. The amount of analyte sorption increases as its concentration increases in the atmosphere. This observation is in good agreement with the predication of the three layer model.

The λ_R shifted 1.45 nm for an isopropanol vapor concentration of 5.5 ppm (parts per million) and shifted as much as 0.7 nm for a toluene vapor concentration of 0.22 ppm. The dependences of λ_R on the analyte vapor concentration are also provided in Fig. 4 and 5, which can be used for quantitative measurement after calibration. The measurement sensitivity and detection limit depend on the type of analyte molecule. For the same concentration, the amount of molecular sorption, sorbate-framework interaction, and molecular sorption-induced changes in zeolite structure and density are different for molecules with different chemical properties such as mass and polarity. These analyte-specific adsorbing behaviors affect the magnitude of variations in refractive index and optical thickness.

The sensor's response time is determined by the equilibrating time of molecular sorption into the zeolite. The response time for isopropanol was less than 2 minutes, which was the time needed for the instrument to complete the scan over the wavelength range. The response time for toluene was about 40 minutes due to its larger molecular kinetic size and low diffusivity in the silicalite zeolite. The zeolite-coated LPFG sensor response had a highly nonlinear relationship with the environmental analyte vapor concentration. This nonlinearity is caused by the dependence of zeolite refractive index on the nonlinear molecular adsorbing behavior [23, 24]. Because most of the zeolites exhibit type-I isotherms characterized by large equilibrium constants in low concentration region the sensor is particularly suited for trace detection. It should be noted that the lowest concentration tested in this study was constrained by the sample gas generation technique used but not the limit for sensor detection.

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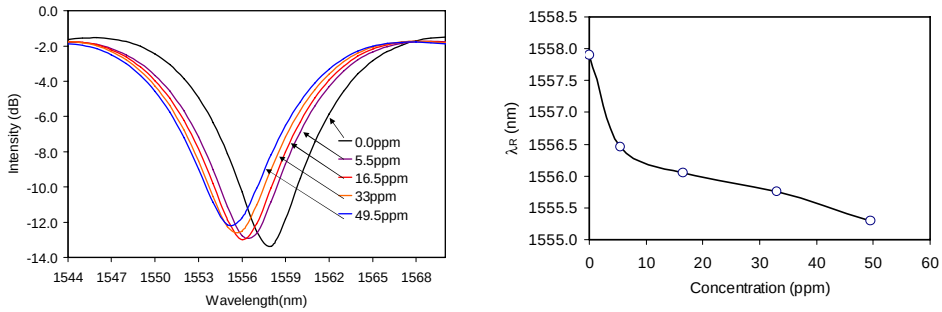

Fig. 4. Displacement of transmission spectrum and λ_R as a function of isopropanol vapor concentration in air.

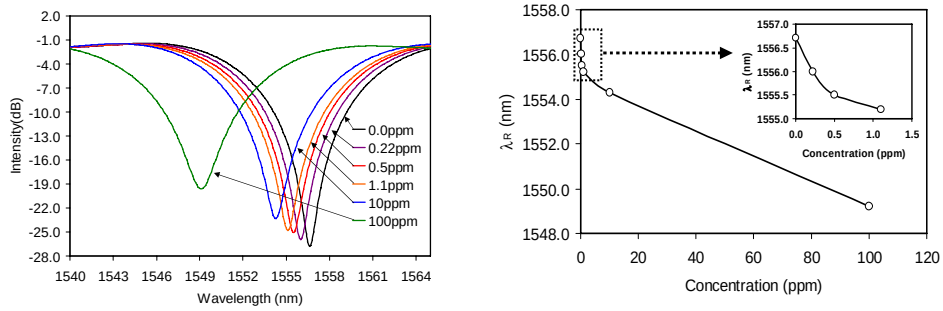

Fig. 5. Displacement of transmission spectrum and λ_R as a function of toluene vapor concentration in air.

4. Conclusion

In conclusion, we demonstrated a zeolite-coated LPFG sensor for highly sensitive chemical vapor detection. The sensor operates by monitoring the molecular adsorption induced refractive index change of the zeolite coating. The zeolite film has multidimensional functions to act as an effective analyte collector/concentrator and an optical chemical probe. With its degassed refractive index around 1.33, the zeolite coating effectively shifts the operating point of LPFG to the region of higher sensitivity upon molecular adsorption. The concept of physically and functionally integrating zeolite films with LPFG may offer new opportunities to develop a variety of chemical sensors for chemical detections with high sensitivities.

Although this study does not focus on the sensor selectivity, there are a number of possible ways to improve the selectivity of the zeolite-LPFG sensors:

Firstly, certain sensing selectivity can be achieved by molecular sieving effect which rejects the molecules with kinetic size larger than the zeolite pore opening. There are more than 100 different types of zeolites with pore size ranging from 3Å to >10 Å that allows of choosing proper pore size for selective sorption of molecules based on their sizes. For complicated gas mixtures, it is also possible to construct a sensor array with a series of zeolite coatings each of which has a pore size appropriate for adsorbing certain molecules. Such molecular sieving effect of zeolite film has been successfully utilized to resolve hydrocarbon selectivity in electrochemical sensors [26].

Secondly, the zeolite internal surface chemistry can be modified to adsorb only a specific type of molecule based on chemical affinity. Such chemisorption can have extremely high selectivity that has been widely employed in chemical industry for removing trace components from ultra pure gases.

Thirdly, the zeolite adsorbing selectivity can be further enhanced by controlling the operating temperature. Different molecules have different sorption strength in the same

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zeolite. The molecular sorption is sensitively affected by temperature. A small increase in temperature may effectively prevent the sorption of weakly adsorbing molecules while keeping high sorption level for strongly adsorbing molecules.

In practical applications, the “pore size selection”, “surface chemistry control”, and “operating temperature adjustment” can be combined to achieve high selectivity of the zeolite-coated sensor.

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